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THE PURPOSES OF THIS REPORT ARE TO:
  1. REVIEW APPLICABLE LITERATURE AND PREVIOUS RMA STUDIES
  2. RECOMMEND A GROUND WATER TREATMENT SYSTEM FOR BASIN F THAT CAN TREAT ORGANICS USING ACTIVATED CARBON AND/OR AN ALTERNATIVE AND IS CAPABLE OF REMOVING CL AND F.
  THE TECHNOLOGIES ARE COMPARED FOR 1) ABILITY TO MEET TREATMENT GOALS, 2) CAPITAL AND OPERATING COSTS, AND 3) TREATMENT FLEXIBILITY.
  FINDINGS AND RECOMMENDATIONS INCLUDE:
  1. BEST ALTERNATIVE TO GAC FOR REMOVAL OF ORGANICS IS UV-CATALYZED OZONATION
  2. BEST METHOD FOR THE REMOVAL OF CL AND F APPEARS TO BE ELECTRODIALYSIS FOLLOWED BY VAPOR COMPRESSION EVAPORATION
  3. BASIN F INTERIM RESPONSE GROUND WATER TREATMENT SYSTEM SHOULD INCLUDE LIME SOFTENING AND MN REMOVAL FOR PRETREATMENT, UV-OZONE AND GAC FOR ORGANIC

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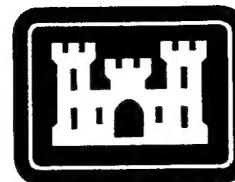
**US Army Corps
of Engineers**

Omaha District

Final Engineering Report

Literature Research & Review Of Groundwater Quality & Treatment Systems For Basin F

Rocky Mountain Arsenal

June 1987

SIRRINE
ENVIRONMENTAL
CONSULTANTS

FINAL ENGINEERING REPORT

LITERATURE RESEARCH AND REVIEW OF
GROUNDWATER QUALITY AND TREATMENT SYSTEMS

FOR
BASIN F
ROCKY MOUNTAIN ARSENAL
DENVER, COLORADO

JUNE 1987
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SIRRINE ENVIRONMENTAL CONSULTANTS **FILE COPY**
GREENVILLE, SOUTH CAROLINA

Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

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SECTION 1

INTRODUCTION

The Rocky Mountain Arsenal (RMA) has been the site of chemical manufacturing, primarily of pesticides and military surety agents, since 1942. Wastes from chemical operations were sent to an asphalt-lined reservoir known as Basin F (Figure 1.1) from 1956 through 1981. Deterioration of the liner allowed organic and inorganic contamination of groundwater that has since migrated off-site. To prevent further contaminant migration, intercepting treatment systems have been constructed on the north, northwest and west boundaries of the arsenal property. Removal of organics at those boundary treatment systems is accomplished with granular activated carbon. No inorganic treatment is performed.

The Corps of Engineers (COE) desires to provide additional treatment of groundwater closer to the source of contamination, namely Basin F. A previous study on groundwater treatment elsewhere at the RMA had established the combination of lime softening and activated carbon as the leading candidate for treating Basin F groundwater.

A progress review meeting (Edgewood Arsenal, 18 May 1987) during this project focusing on applicable technologies resulted in re-directing the purpose of the evaluations. The evaluation did not necessarily need to result in a recommendation of one technology over the other, but rather was to be used to formulate a flexible groundwater treatment facility that might incorporate the two most likely candidate technologies. This approach would allow side-by-side performance and operating comparisons while still achieving the goal of a rapid interim cleanup response at Basin F.

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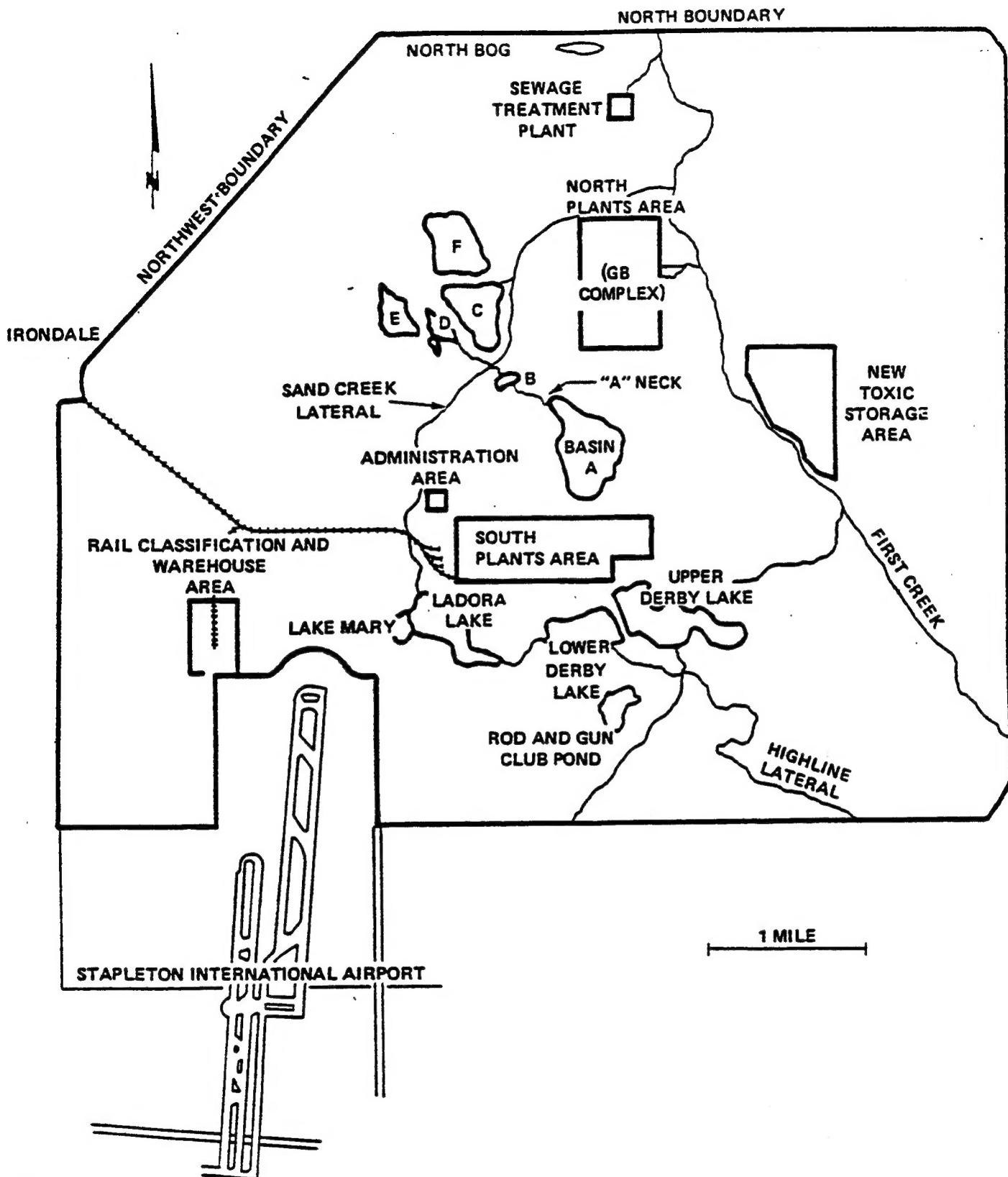
FIGURE 1.1

GENERAL MAP OF ROCKY MOUNTAIN ARSENAL

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Sirrine Environmental Consultants (SEC) was asked to evaluate the original combination of softening and activated carbon and also to conduct a literature search to assist development of an alternative method for treating Basin F groundwater. The two candidate technologies were then to be compared for:

- ability to meet treatment goals
- capital and operating costs
- operability and treatment flexibility.

This report describes the alternative treatment system and the criteria used in its selection.

SECTION 2

SUMMARY

The purpose of this report was to review applicable literature and previous RMA studies and recommend a groundwater treatment system for Basin F that can treat organics using activated carbon and/or an alternative and is capable of removing chloride and fluoride. Inorganic removal is a departure from current RMA groundwater remediation efforts, where dilution, rather than treatment, is used to meet recharge standards. Based on the investigation, the following statements summarize SEC's findings and recommendations:

1) Review of the literature and previous RMA studies indicates the best alternative to granular activated carbon for the removal of the organics of concern at the RMA is UV-catalyzed ozonation.

2) The best method for the removal of chloride, fluoride, and other inorganics appears to be electrodialysis followed by vapor compression evaporation.

3) The Basin F interim response groundwater treatment system should include lime softening and manganese removal for pretreatment, UV-ozone and carbon adsorption for organic removal, and electrodialysis for inorganic removal.

4) Estimated cost for installation of the treatment system is $3,789,000. Estimated operating cost is $1,787,000 per year. These costs are influenced by the higher levels of groundwater contamination at Basin F and the required capability for treatment of inorganic contaminants.

5) The majority of the operating costs are associated with disposal of hazardous residuals generated during treatment.

6) Definition of the groundwater chemical composition, flow rate, and treatment goals is necessary to properly design the interim response treatment facility and develop more accurate cost estimates.

SECTION 3

DESIGN BASIS

The following compounds have been identified by the COE as requiring
treatment in the Basin F groundwater:

Organic

    Aldrin
    Dieldrin
    Endrin
    Composited Sulfur Compounds (CSC)
            p-Chlorophenylmethyl sulfide
            p-Chlorophenylmethyl sulfoxide
            p-Chlorophenylmethyl sulfone
            Dithiane
            Oxathiane
    Dibromochloropropane (DBCP)
    Dicyclopentadiene (DCPD)
    Diisopropylmethyl phosphate (DIMP)

Inorganic

    Chlorides
    Fluorides

Data from alluvial wells immediately north of Basin F were reviewed
for concentrations of these compounds.[1] The period surveyed was
1979-1986, although yearly data was not available for every well.
Referenced wells were:

Section	Wells
23	3, 6, 34, 49, 95, 179
26	8, 9, 11, 15, 16, 45, 46, 125, 133

Organic data was incomplete for many wells and when present often indicated values below the detectable limit. Maximum concentrations were all at or below 5 mg/l. The examined treatment systems are typically insensitive to these influent concentrations, their differences lying in the effluent concentrations that can be achieved. The highest concentrations of aldrin, dieldrin, CSC and DCPD were detected at well 23095. This is the farthest well from Basin F that was examined and was expected to produce some of the lowest values. That it did not suggests retaining the highest concentrations until more representative data is collected. For organic contaminants, therefore, the highest observed concentration was used as the preliminary influent concentration.

As opposed to the organic situation, a large quantity of data was available for chlorides. The highest chloride value was 17,600 mg/l but this was not a representative sample. Influent chloride concentrations in the 1,000-20,000 mg/l range are critical in the selection of treatment processes and the resulting product recoveries and reject concentrations. Based on engineering judgement, a value of 5,000 mg/l is more realistic and would allow evaluation of more treatment technologies.

The maximum fluoride concentration was 10 mg/l. This value typically requires polishing treatment to meet standards and lower concentrations would not affect the process selection. Accordingly, an influent value of 10 mg/l of fluorides will be assumed.

Estimated groundwater concentrations of the compounds to be treated are summarized in Table 3.1. Confirmation of these values will be necessary prior to pilot scale testing.

Drinking Water Standards were used, where available, as effluent guidelines for recharge of the groundwater. Such values exist for chloride, fluoride, DBCP and endrin. For the remaining compounds to

TABLE 3.1

DESIGN BASIS FOR TREATMENT OF BASIN F GROUNDWATER

Parameter	Estimated Influent Concentration	Recharge Limit Concentration	Units
Aldrin	0.78	0.2	ug/l
Dieldrin	6.78	0.2	ug/l
Endrin	23.0	0.2	ug/l
CSC	.992	100	ug/l
DBCP	45.9	0.2	ug/l
DCPD	1333	24	ug/l
DIMP	5030	500	ug/l
Chloride	5000	250	mg/l
Fluoride	10	4	mg/l

Design Flow - 100 gpm

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be treated, the RMA Water Quality Criteria[2] were used. Recharge standards are presented in Table 3.1. These standards and criteria were used to guide the technology selections and evaluations made during this screening process. However, the treatment goals that are established when this interim response facility is installed may not need to be as restrictive as these values presented in Table 3.1. Less restrictive goals for recharge water quality could be justified since the waters will be intercepted and retreated at the existing North Boundary Plant. Furthermore, the Basin F groundwater treatment system will be an interim facility and might best be employed as a means to provide the most cost-effective cleanup of contaminants while comparing more than one technology. Therefore, it may not be economically feasible or desirable to overdesign this interim facility to obtain marginal improvements in removal of some non-critical parameters (e.g., inorganic species).

Background water quality is important in the determination of pretreatment requirements and in the selection of treatment processes themselves. Estimated chemical composition of the groundwater, assembled from the wells listed above, is summarized in Table 3.2. Flow of groundwater to be treated is 100 gallons per minute (gpm). Design life is five years.

TABLE 3.2

ESTIMATED BASIN F GROUNDWATER CHARACTERISTICS

Parameter	Concentration	Units
TDS	12,500	mg/l
Cl^-	5,000	mg/l
Na^+	4,000	mg/l
$SO_4^=$	2,500	mg/l
Ca^{++}	400	mg/l
Mg^{++}	200	mg/l
F^-	10	mg/l
Mn^{++}	2	mg/l
Fe^{++}	Negligible	mg/l
NO_3^-	Negligible	mg/l
Alkalinity	600	mg/l
TOC	50	mg/l
Temp	55-65	°F
pH	6.6-8.0	S.U.

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SECTION 4

REVIEW OF TREATMENT ALTERNATIVES

The primary requirements for a treatment system are that:

1. the effluent (recharge) criteria can be met consistently,
2. it is compatible with the other treatment processes.

Secondary criteria are that:

1. it can be operated with a minimum of process downtime and
2. pretreatment requirements should not be excessive.

ORGANICS

The following technologies were reviewed for their applicability to
the removal of organics of concern in basin F groundwater:

1. Air/steam stripping
2. Chemical precipitation
3. Biological processes
4. Reverse osmosis
5. Polymeric adsorbents
6. Chemical oxidation

Granular activated carbon is perhaps the most consistently applied
method of removing trace, non-volatile organics from groundwater. It
is currently used at the RMA and is the reference to which the
selected alternative treatment will be compared.

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Air/Steam Stripping

Henry's law values (Hc) provide an estimate of the volatility of chemical compounds and, therefore, their potential for air stripping. Values of Hc for DBCP, DCPD, aldrin, dieldrin and endrin were calculated from solubility and vapor pressure data and are presented below. Data for the composited sulfur compounds and DIMP could not be found.

Compound	Hc (dimensionless)
DBCP	1.03×10^{-2}
DCPD	0.335
Aldrin	7.49×10^{-3}
Dieldrin	1.48×10^{-5}
Endrin	2.05×10^{-5}

Except for DCPD, the Henry's constants are too low to achieve recharge standards by air stripping without using excessive air:water ratios. Using steam would increase the volatility of the compounds, but vapor phase carbon adsorption or incineration may still be required to meet air emission limits. Transfer of adsorption from the liquid phase to the vapor provides no economic or technological benefit. Incineration of steam-laden air is difficult and expensive. Stripping, therefore, cannot be considered a realistic treatment option for these organics.

Chemical Precipitation

Precipitation processes involve the formation of insoluble complexes by chemical addition. Organic removal occurs through adsorption on the floc particles, which are settled and dewatered prior to ultimate disposal. This type of fortuitous treatment generally does not achieve the high removal efficiencies required for groundwater recharge and cannot be designed with any certainty. For these reasons, chemical precipitation was not considered for the treatment of organics. Nonetheless, chemical precipitation can still find

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application in groundwater treatment as a pretreatment step or as a mechanism for inorganic removal.

Biological Processes

The organic compounds requiring treatment in the Basin F groundwater are primarily pesticides. These compounds are designed to be persistent in the environment and are very resistant to biodegradation. Biodegradability tests using static-culture shake flasks containing yeast extract and 5 and 10 mg/l of aldrin, dieldrin and endrin individually found no biodegradation of the pesticides in four consecutive 7-day incubation periods.[3] The authors noted that this confirmed other results found in the literature. The U.S. Environmental Protection Agency investigated the treatability of select toxic pollutants and found that biodegradation was not a significant removal mechanism for aldrin, dieldrin and endrin.[4] Futhermore, the total organic content of Basin F groundwater is not sufficient to sustain a sufficient quantity of biomass needed to make biological treatment feasible.

The PACT process uses powdered activated carbon in an activated sludge system to remove inhibitory compounds and to provide sites for biological activity. As the remaining organics in question are not particularly biodegradable, this process would merely be an inefficient method of adsorption. It must be concluded that biological treatment options are not feasible for remediation of the Basin F groundwater.

Reverse Osmosis

Removal of organics by reverse osmosis (RO) has been documented by several researchers. The pesticides lindane, DDT and DDD were reduced 84.0, 99.5 and >99.9 percent by cellulose acetate membranes.[5] A thin film composite (TFC) membrane was found to be superior to polysulfone

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and cellulose acetate membranes in the rejection of total organic carbon (TOC) from tar sand wastewaters.[6] A two-stage RO system was capable of >98% organic and >97% inorganic removal. Aldrin and dieldrin were removed completely by cross-linked polyethylenimine (CLP) membranes and removal by cellulose acetate (CA) membranes was greater than 99%.[7] However, adsorption onto the membrane, rather than rejection, accounted for over 95% of the removal on the CLP membranes and over 75% on the CA membranes. Conversely, another study showed removal of 2,4-D by various membrane types never exceeded 65% even though adsorption was significant.[8]

The latter findings indicate that adsorption onto RO membranes of sparingly soluble organics, such as those in the Basin F groundwater, is a potential problem. Removal effectiveness will decrease as the sorbed substance saturates the membrane. Membrane saturation may also decrease the rejection of other solutes, such as inorganics. A method of membrane regeneration must be found if this occurs.

While RO membranes can be formed to various pore sizes, a lower cutoff for the removal of organic compounds is a molecular weight of 150-200.[9] Molecular weights of DCPD and DIMP are 128.2 and 180.2, respectively, while aldrin and dieldrin are 364.9 and 380.9, respectively. This means that, unless they were adsorbed by the membrane, DCPD and DIMP would partition to the permeate while aldrin and dieldrin would be found in the concentrate. This leaves the need for organic treatment in both streams, an unacceptable situation.

Even if RO membranes could effectively separate all the organic species into the concentrate, final treatment must still be performed. This treatment would be complicated by the high total dissolved solids (TDS) in the concentrate. Incineration would be difficult because of the level of chlorides and fluorides. Concentration by evaporation and crystallization would result in a salt that would probably be considered hazardous. Treatment of the off-gases from the evaporator would be necessary.

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Deficiencies of reverse osmosis in this particular application include organic adsorption, incomplete differentiation of organic species, and the need for ultimate treatment of the organic-laden stream(s). For these reasons, RO is not a feasible treatment technology for organic removal in the Basin F groundwater.

Resin Adsorbents

Resin adsorbents work on the same principle as granular activated carbon (GAC). They come in two types, polymeric and carbonaceous. Resins would have an advantage over GAC if they had a greater adsorption capacity for the organics to be treated, if they were less expensive, if regeneration costs and operator requirements were less, or if the groundwater characteristics preferred their selection. For dieldrin, GAC was found to be more effective than a carbonaceous resin.[10] Resin costs are several times more expensive than GAC.[11] Attrition losses with resins are less than with GAC, but the savings are not enough to make up the difference in initial cost.

Regeneration of resin adsorbents is typically accomplished using steam, caustic, acid or organic solvents. Unless the adsorbate is worth recovering, this creates a liquid stream requiring further treatment. While regeneration of GAC also results in a secondary treatment effort, contaminant removal after thermal regeneration is an integral part of the regeneration system and does not require a separate treatment train.

Resin adsorbents have an advantage over carbon when the chemistry or physical properties of the wastewater indicate better performance with its use. This must be verified by bench-scale testing. The granular activated carbon system currently in use appears to be effectively treating organic contamination, as evidenced by the satisfactory performance reported by the North Boundary Containment/Treatment System.[12]

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Adsorption of organics by resins would be more costly than with granular activated carbon. As the carbon systems currently in use are operating effectively, there is no incentive to replace them with resin adsorbent systems.

Chemical Oxidation

Hydrogen peroxide, potassium permanganate and ozone are the primary chemicals used for the oxidation of organic (and inorganic) contaminants in wastewater. Removal efficiencies of pesticides with hydrogen peroxide were found to be insufficient in an earlier RMA study.[13] Of the three, ozone is the most powerful oxidant[14] and can achieve the greatest removal percentages. Another study at the RMA found ozone in the presence of ultra-violet light to remove 93 percent of DIMP and to lower the concentrations of all other contaminants to below detectable limits.[15] Ozone is therefore the oxidant with the highest potential for treating the Basin F groundwater.

Ozone by itself usually can not achieve quantitative removal of organics without excessive reaction times or ozone dosages. The presence of ultra-violet (UV) radiation is required to catalyze the oxidative reactions and reduce reactor volume and chemical requirements. The destruction of 2-chlorophenol with UV/ozone was found to be significantly faster than with ozone alone.[16]

Ozone is not specific in that it attacks all oxidizable species. Treatment parameters must therefore be based on total organic carbon (TOC).[17] Higher levels of TOC require greater ozone dosages to achieve the same degree of treatment of a particular component that contributes to the combined TOC. Differences in removal percentages among organic compounds arise from their relative ease of oxidation and adsorbability of UV radiation. The results of the previous RMA study suggest that the organics of concern in the groundwater may be preferentially oxidized, thereby reducing the required ozone dosage.

DBCP has been removed to below detectable limits in the treatment of a chemical plant wastewater.[18] High TOC levels made the required ozone dosages too high for economic operation, however. Excellent removal of polychlorinated biphenyls (PCB) in the secondary effluent of a capacitor manufacturer was achieved at more realistic dosages, but no mention was made of the wastewater TOC.[19]

A factor to be considered in organic removal is that complete oxidation, to CO_2 and H_2O, is not economical and probably not necessary.[20] Compounds can be altered to the extent that they are no longer detected analytically without achieving a significant loss of TOC. Whether this is satisfactory treatment depends on the toxicity of the intermediates formed during ozonation. A method of quantifying this is the Microtox biotoxicity analysis.[21] Influent and effluent samples should be analyzed for TOC, Microtox or other procedures such as mutagenicity, and for the specific contaminants of concern when assessing the extent of treatment.

To maximize penetration of the UV light to the organics, scaling on the bulbs and turbidity of the groundwater should be minimized. Pretreatment options include water softening, to remove calcium and magnesium, and filtration.[22] Iron and manganese consume ozone and should be removed upstream. Organic removal is best at neutral pH values[23], although ozone decomposition is a function of pH.[24] This suggests that bench-scale testing needs to be conducted to determine the optimal pH and to avoid over/under sizing of equipment.

A UV-ozone system is currently treating 50 gallons per minute of groundwater contaminated by a wood preserving operation in Nashua, NH.[25] Primary contaminants are pentachlorophenol and creosote. The system has been meeting treatment requirements for approximately six months. No significant operational problems have been experienced. Because the system is automated, operator requirements are approximately only 1/2 hour per day.

The greatest benefit of UV-ozone systems is the absence of
contaminated residuals. There are no side streams or spent adsorbent
requiring further treatment. Other advantages are its low operator
and maintenance requirements. Disadvantages become apparent with
recalcitrant compounds or in high TOC wastewaters when ozone, and
therefore power, requirements become excessive. Significant amounts
of organic material can remain in the ozonated effluent, which may be
a concern for downstream processes. The determination of sufficient
treatment may be difficult if organic destruction is not complete.
Finally, residual (unreacted) ozone in the process effluent may harm
downstream equipment.

UV-ozone is a promising technology for the treatment of low
concentration organics that are non-volatile and non-biodegradable.
It is the recommended method for the removal of organics in the Basin
F groundwater. The main concerns in its application are power
requirements and the level of organic removal that is
achievable/necessary. These questions can best be resolved during
pilot-scale testing.

CHLORIDE REMOVAL

Chloride treatment alternatives include:

1. Evaporation
2. Reverse osmosis
3. Electrodialysis

Precipitation processes are not practical because of the high
solubilities of chlorides. There currently is no treatment of
chlorides in the RMA groundwater.

Evaporation

Evaporation (or distillation) achieves separation of water from
non-volatile solutes by converting the water to steam. The vapor is

then condensed. Total dissolved solids (TDS) in the product water typically ranges between 1 and 500 mg/l. Because of the heating (distillation) and cooling (condensation) requirements, evaporation is an equipment and energy intensive operation. It is therefore quite expensive and is usually economical only when:

1. highly brackish water must be treated,
2. inexpensive heat is available,
3. a very high degree of treatment is required, or
4. contaminants cannot be removed by any other method.[26]

Inexpensive heat is not available. Evaporation could be justified for use with the Basin F groundwater only if the TDS became too high to treat with a membrane process. At this time, the TDS appears to be too low for evaporation to be used as the sole chloride treatment. However, it may have application for the crystallization of concentrate streams from reverse osmosis or electrodialysis systems. Treatment of these smaller flow rates will greatly reduce the power and cooling water requirements dictated by the full-stream system.

Reverse Osmosis

Osmosis is the natural tendency of water to pass through a semi-permeable membrane from the weak solution side to the strong solution side. Pump pressures can be applied to reverse this process and force water from the concentrated side to the pure (permeate) side. This is the basic principle behind reverse osmosis (RO).

Deterioration of the membranes through chemical attack and fouling and plugging of the flow system may make pretreatment necessary. Organic removal, pH control and anti-scalant addition are employed as required by the feed water quality. Pre-filtration to at least 5 microns is required. Corrosion of the process equipment may be a problem, particularly with chloride concentrations above 10,000 mg/l. High chloride levels may dictate higher cost materials of construction. Adsorption of organics onto reverse osmosis membranes is an area of

concern, as has already been stated during the discussion of RO treatment of organics.

Practical operating pressures put limits on the extent of solute concentration that is feasible. RO systems typically have an upper limit of 1000 psig and require 200 psi for a driving gradient, leaving 800 psi as the maximum osmotic pressure of the concentrate solution.[26] Actual operating pressures are usually less because of the high costs dictated by materials of construction and power. Limitations on operating pressure can make high levels of product (feed water) recovery impossible.

Product recovery can also be limited by the concentration of certain inorganic species in the concentrate (brine) stream since precipitation can occur if this concentration becomes too high, resulting in scaling and reduced system performance. Calcium sulfate is typically the precipitate of greatest concern. Upstream softening may be required if calcium and magnesium are present in significant quantities. Sequestrants, such as sodium hexametaphospate, may have to be added to prevent scaling.

Three vendors were given the chemical data in Table 3.2 and asked to suggest a system in which chlorides would be reduced from 5,000 mg/l to 250 mg/l. Product recovery was approximately 50 percent for two of the systems and 75 percent in the third. This low level of recovery can be attributed to the aforementioned limitations on operating pressure and maximum TDS concentration in the concentrate. Such low levels of recovery are unacceptable in this application since they would result in large quantities of residuals that would require further treatment and disposal.

Electrodialysis

Electrodialysis (ED) uses an electric field for the separation of ions into an enriched stream (more concentrated in electrolyte than the original) and a demineralized stream. Synthetic membranes are used to segregate ions by charge, with cation specific membranes allowing passage only of positive ions and anion membranes allowing passage only of negatively charged ions.

Buildup of collected contaminants requires periodic cleaning of the system. This is done automatically by electrodialysis reversal (EDR). Cleaning and descaling of the membranes occurs through reversal of the direct current flow and a simultaneous interchange of diluting and concentrating streams. Softening as a pretreatment step is not necessary but generally increases system capacity and reduces power requirements. Influent iron must be below 0.3 mg/l and manganese must be below 0.1 mg/l. Total suspended solids (TSS) should be less than 2 mg/l.[28] Materials of construction are Schedule 40 PVC. Corrosion is therefore not a problem and equipment costs are reduced.

ED systems operate at low pressures, in the 40 psig range. Their main operating cost is the electricity necessary for separation of the ionic species. Electrical resistance in the ED stacks decreases as the temperature increases. Every 1 deg C increase in operating temperature lowers power consumption by 2 percent.[29]

Because of their lower operating pressures and the fact that organic species tend to pass between the membranes instead of being forced through them, ED systems tend to have less of a problem with organic adsorption than do reverse osmosis (RO) systems. The only organics readily removed by ED systems are those with low molecular weight that can carry a charge, such as short chain carboxylic acids. The organics identified in Table 3.1 for Basin F groundwater should pass through unaffected in an ED system. This is a very important

consideration because it means that the brine, or reject, stream will not contain organic contaminants that would limit disposal options available for those residuals.

Product recovery for an ED system treating the Basin F groundwater is estimated to be 90 percent.[30] Additional recovery is possible but power costs become prohibitive. Nonetheless, recovery by ED is superior to that of RO. Other benefits of ED over RO include no corrosion of equipment, fewer pretreatment requirements and less adsorption of organics. For these reasons, electrodialysis is the recommended method of chloride removal at the RMA.

CHLORIDE DISPOSAL

The reject stream of concentrated salts from the elctrodialysis system is estimated to be 10 gpm based on treating a total through-put of 100 gpm. Hauling nearly 15,000 gallons per day of brine to a landfill would be prohibitively expensive. Consequently, some method of evaporation must be applied to reduce the volume of salts requiring disposal.

Preliminary estimates from conversations with NOAA and EBASCO are that pan evaporation rates of 20-40 inches per year can be expected at the arsenal. For 10 gpm, an evaporation pond would need a surface area of 5-10 acres. If the concentrated salts were considered a hazardous waste, the pond would require a double liner with an intermediate leachate detection system. The pond will most likely have to be demolished after operation of this interim response treatment system is terminated. These two factors offset the apparent low cost of an open pond. Advantages of an evaporation pond are low operator and maintenance requirements, the availability of land and relatively quick installation. Disadvantages are the lack of operational control, seasonal variations in performance, no water recovery, and liner and demolition requirements mentioned above. It may be possible

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to enhance evaporation with a spray system or surface aerator.
Because the RMA does not have water use rights, any water lost to
evaporation.must be replaced with city water.

Placing a cover above the pond would allow recovery of water, prevent
collection of precipitation, and potentially enhance evaporation
rates. Periodic cleaning of the cover would be required, especially
in winter, and the high winds of the Denver area would increase
construction requirements. The additional cost for covering the pond
would have to be recovered within the five year design life.

Another method for concentrating the brine is mechanical evaporation.
Because of the lack of steam at Basin F, a vapor compression
evaporator is recommended. Electricity is the only utility required.
A forced circulation type of evaporator, where the condensate is used
to pre-heat the incoming feed, is recommended to limit scaling. Acid
cleaning may be required periodically for scale removal. Bottoms from
the evaporator are sent to a centrifuge for further concentration of
solids. Filtrate is returned to the evaporator. A bulk handling
system is required for solids removal.

Advantages of the mechanical evaporator are competitive capital costs,
low space requirements, operational control and a salvage value at the
end of treatment operation. Disadvantages include higher operating
and maintenance requirements and the possibility of scaling.
Evaporator costs may increase if the level of fluorides and chlorides
dictate a more resistant material of construction. Delivery of the
evaporator is approximately 6 months ARO, which may not accommodate
the treatment installation schedule.

Concentration of the electrodialysis enriched stream would best be
handled by a vapor compression evaporator. While operating
requirements are greater than with an evaporative pond, capital costs
are comparable, there is greater operational control, and a salvage

value, rather than a demolition liability, exists at the end of the design life. Delivery time for the evaporator may be a concern, however.

A temporary holding area for the evaporator solids prior to disposal will be required. Ultimate disposal will be dependent on the solids classification as a hazardous or non-hazardous waste.

FLUORIDE

Fluoride removal will be a polishing step, because the treatment must only take the concentration from a maximum of 10 mg/l to 4 mg/l. Two of the upstream processes, softening and electrodialysis, are known to remove fluoride. The extent of removal, and therefore the need for final fluoride treatment, must be determined during pilot-scale testing.

Lime softening significantly reduces fluoride concentrations through the formation of sparingly soluble CaF_2.[31] The solubility limit of CaF_2 is 7.8 mg/l, however, and this concentration cannot reliably be achieved because of incomplete solids removal and the effect of other ions. The presence of magnesium can increase the fluoride removal (decrease the solubility of fluoride) through coprecipitation with $Mg(OH)_2$.[32] The high magnesium (200 mg/l) groundwater of Basin F may allow sufficient fluoride removal during softening.

Removal of fluoride in electrodialysis systems parallels the removal efficiency of TDS.[33] Since 90[+] percent removal of TDS is expected, fluoride should be taken from 10 mg/l to less than 1 mg/l. Tertiary removal of fluoride should not be necessary if the ED system is operating as designed. If the ED system is bypassed during testing of the organic treatment alternatives, some method of tertiary fluoride treatment must be available.

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Chemical precipitation methods, such as alum addition or coagulation with iron salts, are difficult to control, generate large quantities of sludge and require very high ratios of chemical to fluoride to achieve the 4 mg/l level[34,35]. The remaining technologies are reverse osmosis and ion exchange. Reverse osmosis will only concentrate the fluoride and further treatment is required. Of the ion exchange processes, the most accepted and proven method of fluoride removal from drinking water is activated alumina.[36] This is the method of choice for treatment of the Basin F groundwater.

Activated alumina (Al_2O_3) is calcined granules of hydrated alumina. It has proven effective in removing fluoride from potable water in Arizona[37] and from feldspar process water.[38] An advantage of activated alumina is that it is fairly specific for fluoride and so has a high exchange capacity. Maximum adsorption capacity occurs at a pH of 5.7.[39] A decrease in adsorption capacity has been observed after continued generation until a steady state is achieved.[40] This indicates that modeling of alumina performance during pilot testing should include multiple regenerations, until a constant fluoride capacity is reached.

Preferred design of activated alumina systems is with dual alternating columns. This arrangement allows one system to be treating the groundwater while the other is being regenerated. Regeneration is manual and is typically performed once a week. One percent caustic (NaOH) solutions are used to regenerate the columns. Re-use of some of the caustic solution may be possible.[41] After two rinses with caustic, the column is neutralized with water at pH 6.8. Sulfuric acid is used to acidify the rinse water. The regenerant solution, containing approximately 500-600 mg/l of fluoride, will be mixed with calcium chloride in a reactor/clarifier for removal of the majority of the fluoride. Attrition losses through regeneration should be approximately 3% when 1% caustic is used.[42]

Arsenic (As) is known to preferentially adsorb onto activated alumina and decrease fluoride capacity. The groundwater analyses referenced in Section 3 indicated very little arsenic in the Basin F groundwater, even though arsenic chloride was produced at RMA by the military.[43] The highest arsenic concentration found was 0.18 mg/l in well 26008. Arsenic at this level will require the use of 4% caustic for regeneration and may necessitate passing the flow through two columns in series.[44]

Activated alumina is capable of effluent fluoride concentrations less than 0.01 mg/l.[45] This may allow treating only a portion of the groundwater and blending the remainder prior to recharge, while still meeting flouride limits. Treating a fraction of the flow will decrease alumina and chemical consumption.

Tertiary removal of fluoride by activated alumina is an effective, proven method for groundwater treatment. It is the recommended technology for use with the Basin F groundwater, if effluent fluoride concentrations would otherwise exceed recharge limits. The primary concern regarding its application is the presence of arsenic.

Pre- and Post-Treatment

The need for pretreatment is governed primarily by the requirements of the electrodialysis (ED) system and UV-ozone reactor. The ED system requires filtration to 2 mg/l of TSS and the removal of iron to 0.3 mg/l and manganese to 0.1 mg/l.[46] Lime softening to remove calcium also allows more reliable ED performance because it reduces the potential for calcium sulfate precipitation in the enriched stream.

Successful operation of UV-ozone is dependent on minimizing both the turbidity of the influent and scaling on the bulbs. This maximizes light penetration and reduces ozone consumption by minimizing the

amount of oxidizable species in the influent. Calcium and magnesium from groundwater systems do not usually cause significant scaling in UV-ozone reactors.[47] Softening of the water may therefore not be necessary. However, manganese and iron exert an ozone demand and should be removed upstream of the UV-ozone unit if possible.

The cold lime softening process has been specified to bring the calcium sulfate precipitation potential to a safer level in the ED enriched stream and to reduce the potential for scaling in the UV-ozone reactor. Manganese and iron removal depends on the level of softening. These metals must be oxidized from their normal divalent states to form precipitates, which are then filtered from solution. Ozone will be used as the oxidant because it will be available, is very powerful and will not cause the formation of undesirable byproducts as chlorine might do. Ozone will be added to the rapid mix tank, where the elevated pH will enhance oxidation of manganese. Precipitated maganese will be removed in a pressurized multi-media filter. The filter also reduces TSS and turbidity to levels required by the ED and UV-ozone systems.

SECTION 5

GROUNDWATER TREATMENT SYSTEM

Based on published technical literature, the goals of this interim
response facility, and the characteristics of the groundwater to be
treated, SEC has formulated a very flexible combination of processes
to treat the Basin F groundwater. It is flexible because it contains
multiple processes that can be employed in series or parallel
sequences to allow performance evaluation of a number of treatability
options.

PROCESS CONFIGURATIONS

A process flow diagram for the groundwater treatment system is
presented in Figure 5.1. For purposes of clarity, all the possible
process configurations that could be implemented have not been shown
in the diagram. Pipe and valve arrangements will allow isolation,
bypassing, reversal, or combination of many of these unit operations.
However, some of the more likely modes of operation are outlined in
Table 5.1. The basic components of the treatment facility include:

- Pretreatment
  . Equalization
  . Lime Softening/Filtration/Recarbonation
  . Associated Solids Handling

- Granular Activated Carbon
  . A small Base-Line GAC System (Control)
  . A Full-Size GAC System
  . Associated Filters

- Alternative Treatment Technologies
  . UV-Ozone for Organics Removal
  . Electrodialysis for Inorganics Control
  . Associated Equipment for Treating Inorganics Residuals
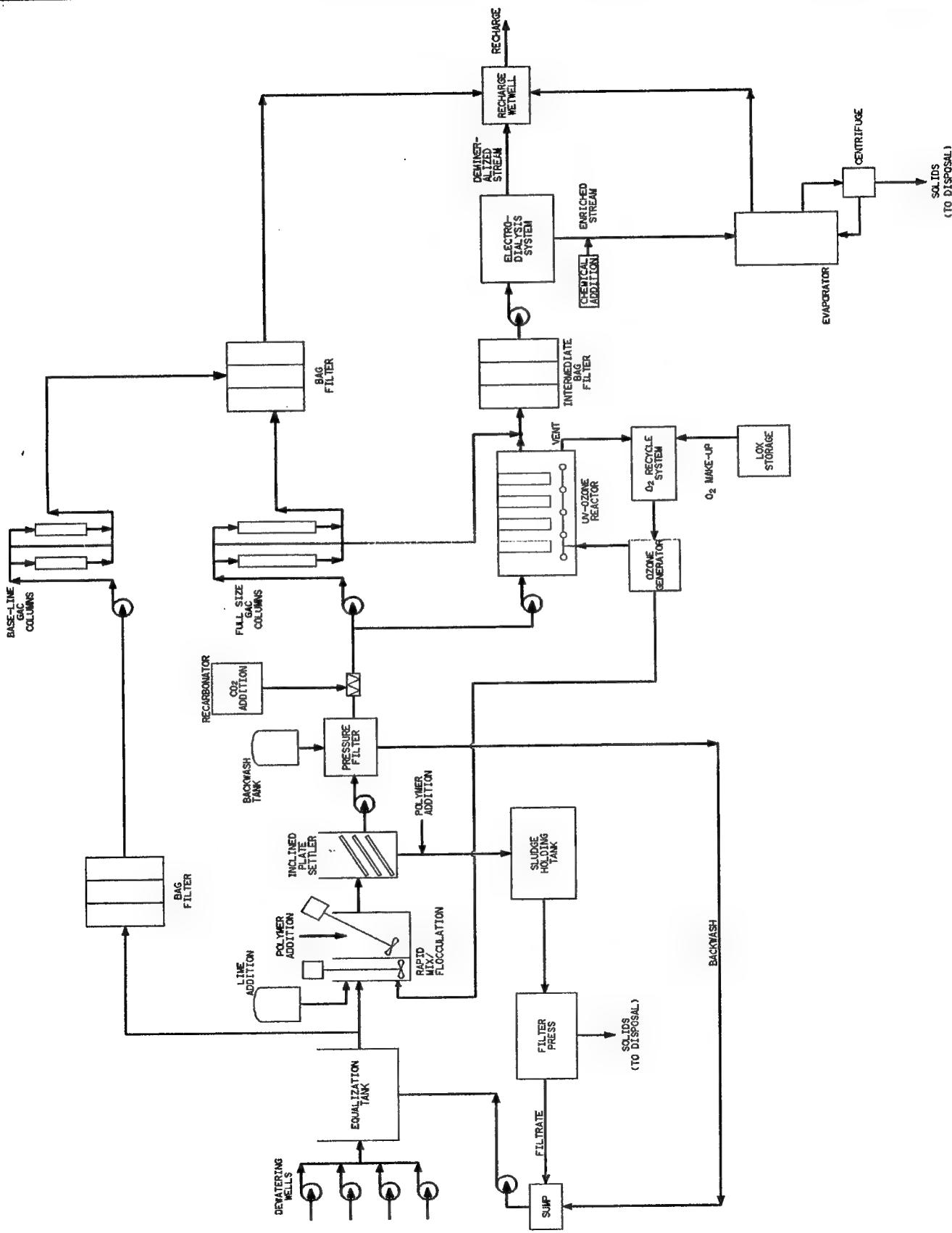
FIGURE 5.1
BASIN F
GROUNDWATER
TREATMENT SYSTEM

COE - ROCKY MOUNTAIN ARSENAL

TABLE 5.1

POTENTIAL PROCESS CONFIGURATIONS

Configuration	Flow (gpm)	Purpose
Base-line GAC only	0-20	Allows comparison with current operations
Softening/Mn Pretreatment, UV-ozone, ED	0-100	Evaluation of suggested alternative in meeting effluent guidelines
Softening/Mn pretreatment, GAC, ED	0-100	Allows comparison with suggested alternative in meeting effluent guidelines
Softening Pretreatment, GAC	0-100	Evaluation of Treatment System No. 1, given by COE
Mn Pretreatment, UV-Ozone	0-100	Evaluation of organics removal by alternative, no inorganic removal but no sludge production
Mn Pretreatment, UV-Ozone, GAC	0-100	Evaluate carbon usage following UV-ozone pretreatment
Softening/Mn Pretreatment, ED, UV-Ozone	0-100	Evaluation of switching order of organic/inorganic removal in process

It will be possible to operate three treatment trains simultaneously, if desired. The small GAC unit may be operated independently of the other two main systems. The second treatment system would be the original candidate technology for this application, the combination of lime softening and activated carbon. Finally, a third treatment train could consist of softening (optional), UV-ozone, and electrodialysis. The softening facility can provide pretreated water to either or both of the two main treatment trains. Those trains can then be operated at 50 gpm or 100 gpm each, depending upon the investigation being pursued by the treatment facility. This option can also be exerised if the character of the groundwater is found to vary over the design life. Another reason to operate more than one treatment train at a time might be to lower total operating costs if a "blend" of treated waters from two systems was found to satisfy recharge treatment goals. Because the system actually contains two treatment trains that can operate at 100 gpm each and a small unit that can process another 20 gpm, it could be possible to produce a maximum output of approximately 220 gpm.

PROCESS DESCRIPTION

The dewatering wells contain integral pumps that send the groundwater to a common collection point. It is assumed that the construction of the wells and pumping systems are the responsibility of another contractor. Associated costs are therefore not included in this report.

Groundwater is collected in a 6,000 gallon mixed tank that gives one hour of retention time. This provides concentration equalization and allows the groundwater to reach equilibrium. Dissolved CO_2 should be nearly completely liberated. thereby reducing the lime requirement in softening. After equalization, flow can be routed either to softening or to a 20 gpm granular activated carbon (GAC) system.

The 20 gpm GAC system provides a base-line comparison with current treatment operations at the arsenal boundary. Groundwater passes through a 50 micron bag filter before the base-line GAC system and through a 10 micron bag filter prior to recharge. This small GAC system will allow two important comparisons to be made. First, can a carbon-only system (no pretreatment) adequately treat the groundwater when intercepted closer to its source? Some previous laboratory studies raised doubts about the effectiveness of GAC when tested on water from well 26008 (i.e. MW-118).[48] Secondly, a side-by-side comparison can be made on any benefits obtained by pretreating with softening prior to GAC. A third benefit is that the overall "production" capability of this interim response treatment facility is increased by 20 gpm.

Softening consists of 5 minutes of rapid mix (500 gallon tank) followed by 30 minutes of flocculation (3,000 gallon tank). Bag lime is slaked prior to addition in the rapid mix tank. Polymer can be added, as necessary, in the flocculation tank to enhance particle formation. The majority of particulate material is removed in an inclined plate settler. Sludge is sent to a holding tank prior to dewatering in a filter press. Filtrate from the press is routed to a sump before being pumped to the equalization tank. A conveyor transports solids cake from the press to a bin prior to disposal. Sludge generation is estimated to be 5700 pounds per day of 25% solids cake.

Clarified overflow from the settler is pumped to a pressurized multi-media filter to remove carryover floc and reduce turbidity and TSS within requirements of the ED and UV-ozone systems. Backwashing of the pressure filter is required twice a day. Water for backwashing is held in a storage tank and backwash is sent to the sump ahead of the equalization tank. Because of the settler, filtration rates of 15 gpm/ft^2 are possible. Oxidation of manganese and iron will be achieved in the softening system. Ozone from the UV-ozone generator

is supplied to the rapid mix tank to oxidize the two metals. The resulting precipitates are removed in the settler and the pressure filter.

The pH must be lowered after softening because the water is usually supersaturated and downstream precipitation could occur. Adjustment of pH may also improve the performance of downstream processes. A recarbonator with feedback control is used to lower the pH. Sulfuric acid was undesirable because of $CaSO_4$ precipitation while hydrochloric acid would contribute chlorides to the water. Therefore, CO_2 cylinders will be used to effect recarbonation by injecting the gas directly into the process stream.

Organic treatment follows softening. Flow can be pumped to either the "full-scale" GAC columns or the UV-ozone reactor or split between them. The GAC system has two columns in series and operates in the down flow mode. Each column has an empty bed contact time of 21 minutes, holds 8,000 pounds of carbon and is sized to treat 100 gpm.

The UV-ozone system consists of two, 50 gpm modules. This allows one unit to be shut down during flow split with the GAC system. Organics in the vented gases are contacted in an aqueous scrubber and returned to the reactor. Oxygen is recycled to the ozone generator. Make-up oxygen for ozone generation, estimated to be 15 percent a day, is supplied by liquid oxygen.

A filter is included between the UV-ozone and ED systems to remove fines that may escape the GAC system. The filter will also remove precipitates formed in the UV-ozone system, although these should be minimal.

Effluent from the GAC and UV-ozone systems can be sent to electrodialysis. The ED system consists of two modules. The first unit generates an enriched stream of 25 gpm and a demineralized stream

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of 75 gpm. The second module reduces the enriched stream to 10 gpm, giving an overall product recovery of 90%. A sequestrant, such as sodium hexametaphosphate (SHMP), may have to be added to the final enriched stream to prevent $CaSO_4$ precipitation.

The enriched discharge from the ED system is sent to a forced circulation, vapor compression evaporator. Concentrate from the evaporator is sent to a centrifuge. Solids from the centrifuge are conveyed to a bin for storage prior to disposal. Sludge generation is estimated to be 24,000 pounds per day of 55% solids content.

Piping allows the ED and UV-ozone system to be reversed in the flow train to optimize treatment performance. Placing ED before UV-ozone may be necessary if inorganics are reducing ozonation significantly. Sufficient fluoride removal should occur in the ED system and therefore activate alumina columns are not included in the design. Activated alumina can be added if fluoride removal by the existing process is unsatisfactory.

Final effluents from the treatment system are comined in an effluent sump prior to recharge. The placement and number of recharge wells is beyond the scope of this report and have not been addressed.

COSTS

Along with performance and operations criteria, the costs associated with various treatment technologies were to be included in this evaluation. Because the recommended interim treatment facility consists of multiple treatment processes that can be combined to assess performance of various modes of operation, SEC has prepared a series of tables that provide a basis for comparison of the different treatment systems to be investigated.

The estimated installed costs of major components are broken out in Table 5.2. Note that no depreciation or salvage values have been factored into these comparative costs. These costs reflect the best judgement available on equipment sizes given that no vendor trials have been performed and the raw water quality and treatment goals still need to be verified. The design bases for sizing most equipment have been presented earlier in the discussion on Process Description. In Table 5.3, other costs associated with constructing the facility are added to installed equipment costs to yield an estimate of the completed facility cost. The engineering services allowance covers engineering design, as well as administration by the Corps of Engineers start-up, and periodic inspection of field operations.

Operational costs for the different technologies are based on a number of factors common to each that have been outlined in Table 5.4. Those factors were used to estimate operational costs for each treatment process as presented in Table 5.5. Items not contained with a discrete process, such as bag filters, were not included because their costs were insignificant in relation to the named processes. Costs are based on 100 gpm of flow through each named process.

The majority of the non-maintenance operational costs (64%) are associated with the disposal of sludge from softening and evaporation. These solids have been assumed to be hazardous, which increases their disposal costs substantially. A dryer could reduce the liquid content of these solids but actual effectiveness cannot be determined without pilot testing. On-site disposal may be a cost effective option if the solids can be determined non-hazardous. Long term liability must be considered in any economic evaluation, however.

Power accounts for 17 percent of the non-maintenance operational costs. The UV-ozone and ED systems account for 98 percent of the power costs. ED power requirements will decrease as the influent TDS decreases or allowable effluent TDS increases.

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TABLE 5.2

INSTALLED EQUIPMENT COST ESTIMATES
FOR
INDIVIDUAL TREATMENT COMPONENTS

Pre/Post Treatment	Cost ($)	
Influent Equalization Tank with Mixer	15 000	
Lime Softening:	100,000	
Lime Feed System Polymer Feed System		
Rapid Mix Tank, Mixer Inclined Plate Clarifier		
Flocculation Tank, Mixer Multi-Media Filter		
Recarbonator	10,000	
Sludge Holding Tank Agitator, Polymer System	27,000	
Sludge Filter Press, Hopper, Conveyor	125,000	
Backwash/Filtrate Sump	8,000	
Recharge Wetwell	5,000	
		290,000
Base-Line Carbon System (20 gpm Control)	90,000	
		90,000
Organics Removal		
Full-Size Carbon System (100 gpm)	220,000	
Bag Filters	15,000	
		235,000
UV-Ozone System	585,000	
Intermediate Bag Filter	5,000	
		590,000
Inorganics Removal		
Electrodialysis System	640,000	
Evaporator, Centrifuge, Conveyor, Bin	500,000	
		1,140,000

TOTAL EQUIPMENT INSTALLED COST = $2,345,000

TABLE 5.3

TOTAL SYSTEM COST ESTIMATE

Installed Equipment Cost (Table 5.2)	$2,345,000
Instrumentation (4%)	94.000
Electrical (inc. substation) (8%)	188,000
Piping (4%)	94,000
Building ($35/sq. ft.)	336,000
Area (roads, fences, etc.)	100,000
TOTAL CONSTRUCTION COSTS =	$3,157,000
ENGINEERING SERVICES (10%)	316,000
CONTINGENCY ALLOWANCE (10%)	316,000
TOTAL SYSTEM COST =	$3,789,000

TABLE 5.4

OPERATING COST FACTORS

Electricity	$0.06/kWh
City Water	$1.50/1000 gallons
Lime	$50/ton
Polymer	$2/pound
Sequestrant (SHMP)	$0.65/pound
Carbon Dioxide	$0.55/pound
Oxygen	$0.45/pound
Sludge Disposal (Hazardous)	$0.10/pound
Granular Activated Carbon (net cost, no regeneration)	$1.10/pound
Labor (includes benefits)	$20.00/hr

TABLE 5.5

ESTIMATED OPERATING COST COMPARISONS

Lime softening/Mn removal
Power	4,000
Chemical	20,000
Labor	22,000
Sludge Disposed	210,000

UV-ozone
Power	52,000
Chemical	12,000
Labor	8,000

Electrodialysis
Power	162,000
Chemical	1,000
Labor	8,000

Evaporator
Power	73,000
Labor	8,000
Sludge Disposal	880,000

Carbon Adsorption
Power	1,000
Carbon Replacement	240.000
Labor	15,000

Process Total	1,716,000
Maintenance @ 3% of Installed Equipment Cost	71,000
Total Operational Costs	$1,787,000/year

Comparison of UV-ozone and carbon adsorption for organics removal
shows a substantial savings with UV-ozone. Carbon costs are primarily
due to carbon replacement. Usage was based on 0.1 pound of TOC per
pound of carbon and 50 mg/l TOC in the influent to the column. This
carbon usage is consistent with values found for Basin F groundwater
in previous RMA studies.[49, 50] UV-ozone costs are based on a 50 mg/l
ozone dosage and 15 percent oxygen make-up. The difference in capital
costs can be recovered in approximately two years. Favorable
economics for the UV-ozone system must be verified by successful field
operations and determination of actual operating requirements.
Analytical costs have not been considered. Pilot testing of this
order, involving trace organic compounds, will require considerable
laboratory work and this cost must be anticipated.

SECTION 6

CONCLUSIONS

Applicable literature and previous RMA studies were reviewed in the search for alternative technologies for the treatment of Basin F groundwater. This review resulted in the selection of a multicomponent system that allows numerous process options in the treatment of 100-220 gpm of groundwater. The proposed treatment system differs from current groundwater remediation efforts at the RMA in that quantitative removal of inorganics is possible and the raw water will contain higher levels of contaminants than observed at the boundary treatment systems.

Lime softening and oxidative manganese removal may be employed as pretreatment processes. Carbon adsorption and UV-catalyzed ozonation are specified as alternative technologies for the removal of organics. Inorganics, particularly fluoride and chloride, are separated from the product water using electrodialysis and further concentrated in an evaporator and centrifuge.

Comparison of various treatment configurations is facilitated by bypass, isolation and reversal piping options, and the flexible nature of the selected process equipment. A parallel treatment system consisting only of carbon adsorption with pre- and post-filtration provides a basis of comparison with current groundwater remediation efforts.

Installed costs for the system, including equipment construction, and engineering are estimated to be $3,789,000. Operational costs are estimated to be $1,787,000 per year for operation of both treatment trains at full capacity (200 gpm). These apparently high costs must be viewed in perspective. Basin F groundwater has a higher level of

both organic (TOC, specific compounds) and inorganic contamination than is found at the boundary treatment systems. Dedicated treatment of inorganics is being addressed for the first time, which contributes substantially to the capital costs. Disposal of hazardous residuals, which are primarily the result of treatment of inorganics, constitutes the majority of operating costs. For treatment of organics, however a UV-ozone system offers substantial operational cost savings over an activated carbon system. These savings must be confirmed through successful removal of the organics of concern by UV-ozone and quantification of actual operating costs for both systems.

Process design and cost estimates are based on data from alluvial wells north of Basin F taken over the last seven years. Chemical composition of the groundwater must be verified by sampling new wells in the estimated area where dewatering will occur before the treatment system and associated costs can be finished.

SECTION 7

RECOMMENDATIONS

Based on the available data, treatment experience already gained at the RMA, and the evaluations accomplished in this project, SEC recommends that combinations of the following treatment processes be used to treat Basin F groundwater:

- Lime softening
- Granular activated carbon
- UV-ozone oxidation
- Electrodialysis.

These technologies should be integrated into an interim response treatment facility that will allow process optimization while achieving quantitative remediation of Basin F groundwater contamination without the delays associated with experimental studies.

To implement this recommendation, the following tasks should be accomplished to assure that the facility is properly designed to meet the needs of the interim response action.

a) Determine approximate location of dewatering wells for the treatment system. Collect alluvial well samples and analyze for the contaminants of concern given in Section 3 as well as for TOC, TDS, Ca^{++}, Mg^{++}, SO_4, alkalinity, MN^{++}, Fe^{++}, and heavy metals.

b) Define dewatering capacity of aquifer and confirm design flow rate for the interim treatment facility.

c) Redefine treatment goals, if necessary.

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d) Examine other disposal alternatives for residuals versus placement in a hazardous waste landfill.

e) Confirm treatment equipment performance, requirements and cost by short-term trials. Develop refined capital and operating costs.

f) Define remediation schedule. Develop detailed design and get bids for equipment purchase, delivery, and installation.

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